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Cite as: J. Chem. Phys. **105**, 4117 (1996); https://doi.org/10.1063/1.472282
Submitted: 26 April 1996 • Accepted: 06 June 1996 • Published Online: 31 August 1998

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Thermally activated escape processes in a double well coupled to a slow harmonic mode

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(Received 26 April 1996; accepted 6 June 1996)

We present accurate calculations of thermally activated rates for a symmetric double well system coupled to a dissipative harmonic mode. Diffusive barrier crossing is treated by solving the time-independent two-dimensional Smoluchowski equation as a function of a coupling and a diffusion anisotropy parameter. The original problem is transformed to a Schrödinger equation with a Hamiltonian describing a reactive system coupled to a one-dimensional harmonic bath. The calculations are performed using a matrix representation of the Hamiltonian operator in a set of orthonormal basis functions. An effective system-specific basis is introduced which consists of adiabatically displaced eigenfunctions of the coupled harmonic oscillator and those of the uncoupled reactive subsystem. This representation provides a very rapid convergence rate. Just a few basis functions are sufficient to obtain highly accurate eigenvalues with a small computational effort. The presented results demonstrate the applicability of the method in all regimes of interest, reaching from inter-well thermal activation (fast harmonic mode) to deep intra-well relaxation (slow harmonic mode). Our calculations reveal the inapplicability of the Kramers–Langer theory in certain regions of parameter space not only when the anisotropy parameter is exponentially small, but even in the isotropic diffusion case when the coupling is weak. The calculations show also that even for large barrier heights there is a region in the parameter space with multiexponential relaxation towards equilibrium. An asymptotic theory of barrier crossing in the strongly anisotropic case is presented, which agrees well with the numerically exact results. [S0021-9606(96)52534-1]

I. INTRODUCTION

The diffusional theory of chemical reactions established by Kramers[1] is one of the prominent advances of classical rate theory. It provides an approximate and often very useful statistical model of thermally activated barrier crossing processes. Its fundamental underlying assumption is that a chemical reaction is modeled by the motion of a Brownian particle with mass weighted reaction coordinate x in a bistable potential of mean force $U(x)$, i.e.,

$$\ddot{x} = -U'(x) - \eta\dot{x} + \sqrt{2\eta/\beta}f(t), \tag{1}$$

where the dot denotes the time derivative, and the prime the derivative with respect to the coordinate. The solvent influences the reaction coordinate by a velocity-proportional damping force $-\eta\dot{x}$ and a fluctuating force $\sqrt{2\eta/\beta}f(t)$ which is Gaussian and uncorrelated on the time scales defined by the potential and the damping force. In his discussion Kramers clearly distinguished between the small and the large damping ranges. He showed that the reaction rate depends nonmonotonically on the damping constant η; it increases at small damping (in the energy-diffusion controlled regime) and eventually falls off with the damping constant when the latter becomes large enough to ensure Boltzmann equilibrium (in the spatial-diffusive regime). In the strong damping limit, the position of the particle completely describes the state of the system, and the process is governed by the following Smoluchowski equation for the probability density $P(x,t)$ of finding the particle at time t at position x:[1]

$$\partial_t P(x,t) = (\beta\eta)^{-1}\partial_x e^{-\beta U}\partial_x e^{\beta U}P(x,t), \tag{2}$$

where ∂_x denotes the partial derivatives with respect to x.

Kramers' model (1), although simple, is of enormous utility in understanding and evaluating the influence of the medium on reaction rates. It has found various generalizations,[2] for example, to cases with many degrees of freedom,[3,4] generalized Langevin equations,[5] unified Kramers-turnover[6–8] (for a recent review see also Ref. 9) and systems without detailed balance.[10–13] In all these investigations, however, the height of the potential barrier ΔU is assumed to be sufficiently large when compared to the energy of thermal motion β^{-1}. Yet another fundamental assumption which is almost always made is that the inverse transition rate over the barrier is the largest relaxation time of the considered system. However, these assumptions are not always met in real physical and chemical barrier crossing processes. Often the potential barrier is not extremely large. For example, the activation energy of isomerization processes in a condensed phase is often of the order $5\beta^{-1}$. In such cases, Kramers theory gives only approximate results. Large deviations from Kramers theory and even its complete-failure may occur if the considered problem contains other small quantities except $(\beta\Delta U)^{-1}$.

Such a situation may arise if the heat bath contains slowly relaxing modes which influence the dynamics of the reactive subsystem in a more complicated fashion than the

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conventional Brownian motion picture implies. A charge transfer reaction in a polar solvent with a slowly relaxing polarization provides an example of a reactive system with a slow nonreactive mode. In this case, the influence of the nonequilibrium solvation on the reaction dynamics can be properly described by an additional solvation coordinate y that interacts with the reaction coordinate according to the following coupled Langevin equations:[14]

$$\begin{aligned}\ddot{x} &= -\partial_x V(x,y) - \eta_x \dot{x} + \sqrt{2\eta_{x/\beta}} f_x(t),\\ \eta_y \dot{y} &= -\partial_y V(x,y) + \sqrt{2\eta_y/\beta} f_y(t),\\ V(x,y) &= U(x) + \frac{\Gamma}{2}[y - y_{\mathrm{eq}}(x)]^2,\end{aligned} \tag{3}$$

where $U(x)$ is a bistable potential of mean force, $y_{\mathrm{eq}}(x)$ the equilibrium value of the solvation coordinate at a fixed value of the reaction coordinate, Γ the coupling constant (and at the same time the bath frequency), and $f_x(t)$ and $f_y(t)$ denote uncorrelated zero mean Gaussian white noises. In a series of papers,[15] Berezhkovskii and Zitserman have demonstrated that considerable deviations from the Kramers–Langer theory,[4] which is the standard multidimensional generalization of the Kramers theory, may occur in the highly anisotropic limit $\eta_y \gg \eta_x$. In the particular case with $\eta_x = 0$ such deviations had been observed already earlier.[7,16,17] Both problems have been studied very actively in recent years. Finite barrier corrections of the rate have been obtained in a number of papers.[11,18–21] Various different methods have been proposed to generalize the Kramers–Langer theory to the case of strongly anisotropic diffusion.[15,22,23]

Though there are also numerical studies of the anisotropic diffusion problem,[24,25] a detailed understanding of the range of validity of the Kramers–Langer rate expression is still lacking. In particular, it has remained unclear whether the deviations between the Kramers–Langer rate and the true rate grow slowly with increasing anisotropy, or set in abruptly at a certain value of the anisotropy parameter. The lack of answers to these questions is not surprising because almost all numerical investigations[24] are based on conventional time-dependent grid based propagation schemes which are generally inappropriate for the present purpose. Of course, it is possible to extract the escape rate from the time evolution of the distribution function,[9,24] but in the strongly anisotropic limit, calculations over very long times are required. Conventional basis set methods[25] only give satisfactory results for nearly isotropic diffusion or in cases of rather low barriers. Even for not so high barriers, say $\beta\Delta U \geqslant 5$, the standard basis set of unscaled harmonic oscillator eigenfunctions converges slowly, and its rate of convergence rapidly decreases with increasing diffusion anisotropy, i.e., when the bath mode becomes slow. It is then difficult to obtain precise numerical values of the escape rate, and almost impossible to analyze a multiexponential decay. A different approach is based on an effective system-specific set of nonorthogonal basis functions.[26] Although this method allows one to properly incorporate the coupling between the system and the bath mode, it requires a full matrix representation of the Hamiltonian operator. As a result, with increasing diffusion anisotropy the storage requirements and execution time grow rapidly, in order to attain a desired level of accuracy.

In this paper, we develop a numerical method which is free of the mentioned drawbacks. It yields the low lying eigenvalues of the considered Smoluchowski equation in the whole parameter range up to a given level of accuracy. With increasing accuracy the necessary numerical effort grows only weakly. Further, we present a simple asymptotic theory of barrier crossing for the case of a slowly relaxing bath mode which is based on an adiabatic elimination of the fast reactive coordinate. And finally, the main purpose of the present work is to reveal the range of validity of the Kramers–Langer theory for this archetypical model of a coupled reactive and relaxational mode in the overdamped regime. Both the model and the asymptotic theory of barrier crossing in the limit of the slow bath are presented in Sec. II. The numerical method is described in Sec. III. In Sec. IV we present our numerical results for the spectrum of eigenvalues for different temperatures, coupling constants and anisotropy parameters. The numerical results are compared to both the predictions of the asymptotic theory and to the Kramers–Langer theory. Sec. V concludes with final remarks and an outlook.

II. THEORY OF BARRIER CROSSING

In this section, we first present the model we are going to study, and then an asymptotic theory for treating a slowly relaxing bath mode.

A. Model

We discuss the model defined in Eq. (3) in the limit of strong damping in both x- and y-direction. It consists of a reactive and a relaxational mode, which both undergo a diffusional motion with generally different diffusion constants. There are various different processes such as charge-transfer reactions in polar solvents,[14,27] stilbene isomerization in a condensed phase,[28] and binary homogeneous nucleation,[29] to name only a few in which an anisotropy of the diffusion can significantly influence the reactive dynamics and which can be described by such a model. In dimensionless variables the dynamics is given by the Smoluchowski equation[14]

$$\begin{aligned}\partial_t P(x,y,t) = D(&\partial_x e^{-V/D} \partial_x e^{V/D}\\ &+ \epsilon \partial_y e^{-V/D} \partial_y e^{V/D}) P(x,y,t),\end{aligned} \tag{4}$$

where the potential is given by

$$\begin{aligned}V(x,y) &= U(x) + \frac{\gamma}{2}(y-x)^2,\\ U(x) &= \tfrac{1}{4}x^4 - \tfrac{1}{2}x^2.\end{aligned} \tag{5}$$

Here, D is a dimensionless temperature, $D = 4(\beta\Delta U)^{-1}$, the anisotropy parameter $\epsilon = \eta_x/\eta_y$ is the ratio of the damping coefficients in the direction of system and bath coordinates x and y, respectively, and time is measured in units of η_x^{-1}. The potential $V(x,y)$ has two minima at $(-1,-1)$ and $(1,1)$

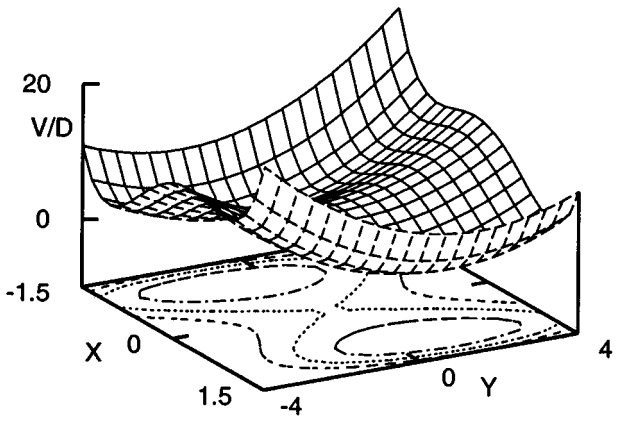

FIG. 1. Potential surface $V(x,y)/D$ [Eq. (4)] and its equipotential lines for $D=0.05$, and $\gamma=0.05$.

and a transition point at the origin. A typical shape of the potential surface and the corresponding equipotential lines are shown in Fig. 1.

For a wide range of parameters, the equilibration process of this systems is determined by the transition rate from one well into the other. In a symmetric potential the least nonvanishing eigenvalue of the corresponding Smoluchowski operator is then given by twice this rate.[30] Therefore, applying the Kramers–Langer theory[4] to the process (4), one immediately obtains an approximate expression for this eigenvalue. It has the form of an Arrhenius law reading

$$\lambda_1=\frac{\sqrt{2}}{\pi}\,\kappa\,\exp\{-E\}, \tag{6}$$

where $E\equiv\beta\Delta U=(4D)^{-1}$ is the activation energy in thermal units, and κ the transmission factor reading

$$\kappa=\tfrac{1}{2}\{1-\gamma-\gamma\epsilon+[(1-\gamma-\gamma\epsilon)^2+4\gamma\epsilon]^{1/2}\}. \tag{7}$$

It determines the behavior of the least eigenvalue as a function of γ and ϵ. We note that in the original variables, used in Eq. (3), the rate is proportional to $1/\eta_x$, and, hence, is always small. A simple analysis of Eq. (7) shows that the transmission factor tends to unity for all positive γ's if the anisotropy parameter goes to infinity. On the other hand, in the limit of vanishingly small anisotropy parameters (we will denote this limiting case as the *strongly anisotropic limit*) there are three regimes with different dependence of λ_1 on ϵ. When γ is larger than unity, λ_1 linearly tends to zero with decreasing ϵ, i.e., as $\kappa\simeq\epsilon\gamma/(\gamma-1)$. For $\gamma=1$ it goes to zero as $\sqrt{\epsilon}$, and for $\gamma<1$ the transmission factor goes to a finite value, namely $\kappa=1-\gamma$. However, this does not correctly describe the behavior of the least nonzero eigenvalue of the Smoluchowski equation which is governed by the dominant slow y-motion in the strongly anisotropic limit. Thus, we expect considerable deviations of the predictions of the Kramers–Langer theory from numerically exact results for the least eigenvalue in the limit $\epsilon\to 0$ for positive $\gamma\leqslant 1$. We note that the potential profiles $V(x,y=\text{const})$ at fixed values of y have a single well or two wells depending on whether γ is larger or less than unity.

The above observations are in agreement with a theory developed by Berezhkovskii and Zitserman which corrects Langer's result in the case of strongly anisotropic diffusion.[15] According to this theory the main criterion of the validity of Langer's formula is the shape of the potential surface. If $V(x,y)$ has only single well sections $V(x,y=\text{const})$, Langer's formula is valid for all ϵ. On the contrary, if the potential has double well profiles, Langer's formula is only applicable if the y mode is not too slow, and fails to produce correct results in the limit $\epsilon\ll 1$. It is worth noticing that little is known how small ϵ must be, in order that the Kramers–Langer theory fails. Our calculations confirm the qualitative picture of Berezhkovskii and Zitserman. However, we find that for small values of ϵ the deviations from the Kramers–Langer theory start to show for values of γ which are larger than unity and continuously grow with decreasing γ.

Finally we note that also for small values of γ the Kramers–Langer theory does not give the least nonzero eigenvalue, since then the y-mode becomes slow and a ladder of equally and densely spaced harmonic oscillator eigenvalues determines the spectrum near zero. On the other hand, in this limit the reactive and nonreactive modes almost decouple, and, therefore, the slow relaxation of the y mode has little influence on the reactive dynamics of the x mode.[23] In the next subsection we consider the limiting cases of both small ϵ and small γ.

B. The limit of slowly relaxing bath mode

The exact solution of the Smoluchowski equation (4) can formally be represented in terms of the set of functions $\{\Phi_m(x,y)\}$,

$$P(x,y,t)=\sum_{m=0}^{\infty} P_m(y,t)\Phi_m(x,y), \tag{8}$$

which are eigenfunctions of the operator

$$L_x=D\partial_x\,\exp\{-V(x,y)/D\}\partial_x\,\exp\{V(x,y)/D\}, \tag{9}$$

with the variable y considered as a parameter. The eigenvalue problem reads

$$L_x\Phi_m(x,y)=-\mu_m(y)\Phi_m(x,y), \tag{10}$$

where $\mu_m(y)$ is the eigenvalue belonging to $\Phi_m(x,y)$. The corresponding adjoint problem is

$$L_x^{+}Q_m(x,y)=-\mu_m(y)Q_m(x,y). \tag{11}$$

Since L_x has the structure of a one-dimensional Smoluchowski operator [cf. Eq.(2)], all eigenvalues $-\mu_m(y)$ are real and less than or equal to zero. The zero eigenvalue $\mu_0=0$ is in general nondegenerate. The respective eigenfunctions read

$$Q_0(x,y)=1,$$
$$\Phi_0(x,y)=\exp\{[V_e(y)-V(x,y)]/D\}, \tag{12}$$

where $V_e(y)$ denotes an effective potential[15,23] reading

$$V_e(y) = -D \ln \int_{-\infty}^{\infty} dx \, \exp\{-V(x,y)/D\}. \tag{13}$$

The left- and right-eigenfunctions $Q_m(x,y)$ and $\Phi_m(x,y)$ constitute a biorthogonal set of functions

$$(Q_m, \Phi_n)_x = \delta_{m,n}, \tag{14}$$

where $(\ ,\ )_x$ denotes a scalar product of functions of x

$$(f,g)_x = \int dx f(x) g(x). \tag{15}$$

Putting Eq. (8) into Eq. (4), multiplying with $Q_n(x,y)$ and integrating over x, one obtains a set of equations for the coefficients $P_n(y,t)$

$$\partial_t P_0(y,t) = \epsilon \left[L_e P_0(y,t) + \sum_{m=1} (Q_n, L_y \Phi_m)_x P_m(y,t) \right], \tag{16}$$

$$\partial_t P_n(y,t) = -\mu_n(y) P_n(y,t) + \epsilon \sum_{m=0} (Q_n, L_y \Phi_m)_x P_m(y,t), \quad n \geq 1, \tag{17}$$

$$L_y = D \partial_y \exp\{-V(x,y)/D\} \partial_y \exp\{V(x,y)/D\}, \tag{18}$$

where L_e describes the motion in y direction in the potential of mean force $V_e(y)$ defined by Eq. (13)

$$L_e = (Q_0, L_y \Phi_0)_x = D \partial_y \exp\{-V_e(y)/D\} \partial_y \times \exp\{V_e(y)/D\}. \tag{19}$$

Since the $\mu_n(y)$ are independent of the anisotropy parameter, one can neglect the second contribution of the right hand side of Eq. (17) in the asymptotic limit $\epsilon \to 0$. One obtains in this way decoupled equations for the coefficients $P_n(y,t)$, $n \geq 1$, which relax to zero much faster than $P_0(y,t)$ changes. Hence, in the small-ϵ limit, the long-time behavior of the two-dimensional process (4) is governed by the one-dimensional Smoluchowski equation

$$\partial_t P_0(y,t) = \epsilon D \partial_y \exp\{-V_e(y)/D\} \partial_y \times \exp\{V_e(y)/D\} P_0(y,t). \tag{20}$$

In the same limit, an equivalent equation for the mean first passage time to the line $y=0$ was derived in Ref. 22. In contrast to Refs. 15 and 24 no source term is present in the Smoluchowski equation (20). In principle, corrections of higher orders in ϵ can be included in Eq. (20), but we will not do so here. The relevant time scale describing the long time behavior of $P_0(y,t)$ is given by the first nonzero eigenvalue of the Smoluchowski operator ϵL_e which crucially depends on the shape of the effective potential V_e. As is seen from Fig. 2, this potential has either a single minimum or two minima depending on the parameters γ and D. Thus for instance, if the coupling constant is sufficiently large, $\gamma \gg U''(x_{\min}) = 2$, the most dominant part of the potential $V(x,y)$ is the interaction $(\gamma/2)(x-y)^2$ which favors $x=y$. Hence, in this limit one finds

$$V_e(y) = U(y). \tag{21}$$

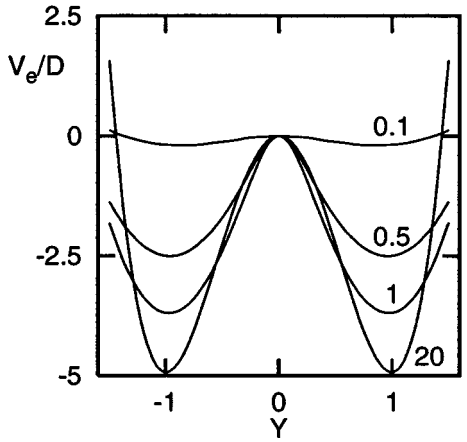

FIG. 2. Effective potential $V_e(y)/D$ [Eq. (20)] for $D=0.05$, and $\gamma=0.1$, 0.5, 1, and 20.

With decreasing coupling strength at a fixed value of D the potential V_e becomes wider, and the barrier flattens. For small D and γ, $\gamma = \mathcal{O}(D)$, a Gaussian approximation of the integral in Eq. (13) about the minima of the potential $U(x)$ yields

$$V_e(y) = \frac{\gamma}{2} y^2 - D \ln \cosh \frac{\gamma}{D} y, \tag{22}$$

which has two wells for $\gamma > D$ and a single well otherwise.

In the case of a symmetric double well, the least eigenvalue is given by the mean first passage time for the y-process starting at one of the local minimum values, say, at $y=-1$, to reach the top of the barrier at $y=0$[30]

$$\lambda_1^0 = D\epsilon \left\{ \int_{-1}^{0} dy \int_{-\infty}^{0} du \, \exp\{[V_e(y) - V_e(u)]/D\} \right\}^{-1}, \tag{23}$$

where the superscript ''0'' indicates that the formula is valid in the small-ϵ limit. For large γ we find with Eq. (21)

$$\lambda_1^0 = \epsilon \lambda_1^{\infty}, \tag{24}$$

where λ_1^{∞} is the least eigenvalue for $\epsilon \to \infty$, in which case the one-dimensional activated process in the x direction determines the slow dynamics. Consequently, λ_1^{∞} reads

$$\lambda_1^{\infty} = D \left\{ \int_{-1}^{0} dx \int_{-\infty}^{0} du \, \exp\{[U(x) - U(u)]/D\} \right\}^{-1}. \tag{25}$$

In the single well case, the least eigenvalue describes the relaxation of the slow y mode. The effective potential $V_e(y)$ is then approximately parabolic with curvature γ, and, therefore, the least eigenvalue becomes

$$\lambda_1^0 = \epsilon \gamma. \tag{26}$$

Since the next eigenvalue is only approximately $2\lambda_1^0$, no pronounced gap exists and the long time behavior is generally multiexponential.[15] This means that a rate description of the long time dynamics is inappropriate in this case.

Finally, we want to determine a critical value ϵ_c above which the one-dimensional Smoluchowski equation (20) for the y mode fails to describe the original two-dimensional process (4). For this purpose we compare the least eigenvalues λ_0^1 and λ_1^∞ of the one-dimensional Smoluchowski equations which describe the process correctly in the limits of small and large ϵ, respectively. If the coupling between the system and bath mode is strong, $\gamma \gg U''(x_{\min})$, Eq. (24) holds and, hence, $\epsilon_c = 1$. In the range of intermediate coupling strength $\gamma \sim U''(x_{\min})$, the effective potential $V_e(y)$ still has two minima, and the eigenvalues λ_1^0 and λ_1^∞ are the same when ϵ assumes the critical value ϵ_e reading

$$\epsilon_c = \frac{\int_{-1}^{0} dy \int_{-\infty}^{0} du \, \exp\{[V_e(y) - V_e(u)]/D\}}{\int_{-1}^{0} dx \int_{-\infty}^{0} du \, \exp\{[U(x) - U(u)]/D\}}. \tag{27}$$

By construction, for $\epsilon > \epsilon_c$ the one-dimensional Smoluchowski equation (20) fails. Numerical calculations of the spectrum of eigenvalues of the two-dimensional equation (4) which are presented in more detail in Sec. IV show that the rough estimate (27) gives a surprisingly good criterion for the validity of Eq. (20). Moreover, the numerical calculations show that the transition to a one-dimensional description happens in a smooth way within an order of magnitude around ϵ_c. This means that for $\epsilon < \epsilon_c$ Eq. (20) well describes the long time behavior of the full process whether it is governed by a single rate or is multi-exponential.

Multiexponential decay occurs in the limit of weak coupling, $\gamma \leqslant D$, in which $V_e(y)$ has only a single minimum. Comparing Eqs. (25) and (26) yields for the critical anisotropy parameter

$$\epsilon_c = \frac{1}{\pi \gamma} \sqrt{U''(x_{\min}) |U''(x_{\max})|} \exp\{-E\}, \tag{28}$$

where for small D the integrals in Eq. (25) have been evaluated in Gaussian approximation.

It is clear that for $\epsilon < \epsilon_c$ the true rate strongly deviates from the Langer formula when the barrier of the effective potential $V_e(y)$ is smaller than that of the original system potential $U(x)$. This is the case for $\gamma \leqslant U''(x_{\min})$. When γ is comparable or even smaller than the diffusion coefficient D, $\gamma \leqslant D$, the dynamics becomes barrierless and the rate constant description is no longer appropriate even though the bare potential height might be large. In principle, the value of ϵ_c can very well be larger than unity also in the latter case of the purely relaxational dynamics, but then γ is exponentially small and the reactive and relaxational modes decouple. On the other hand, we want to emphasize that the Kramers–Langer theory gives the correct rate when either of the following two conditions is violated

$$\gamma \leqslant U''(x_{\min}), \quad \epsilon \leqslant \epsilon_c. \tag{29}$$

Closing this section, we note that the presented asymptotic theory admits an obvious generalization to the multidimensional Kramers–Langer problem with an arbitrary nonlinear coupling between the system and the bath modes.

III. NUMERICAL METHODS

In this section, two efficient methods for the numerical solution of time-independent Smoluchowski and Schrödinger equations are developed. First we present a variational approach which is very efficient in dealing with a so-called system-bath situation in which a nonlinear degree of freedom couples to another harmonic one. We use this method for solving the original two-dimensional problem (4). For the solution of the one-dimensional Smoluchowski equation (20) with the potential defined in Eq. (13) we use a finite-difference method which is presented in the second part of this section.

A. A variational procedure

For the sake of generality, we consider a nonlinear coupling between the reactive system and the harmonic bath

$$L = D(\partial_x e^{-V/D} \partial_x e^{V/D} + \epsilon \partial_y E^{-V/D} \partial_y e^{V/D}),$$

$$V(x,y) = U(x) + \frac{\gamma}{2}[y - g(x)]^2, \tag{30}$$

where the coupling function $g(x)$ can have an arbitrary form. First, we transform Eq. (30) by means of the ansatz

$$P(x,y,t) = \psi(x,y,t) \exp\left\{-\frac{V(x,y)}{2D}\right\} \tag{31}$$

into a Hamiltonian operator of the system–bath form

$$H = H_x + H_y + H_{xy}, \tag{32}$$

where H_y describes the bath, H_x the system, and H_{xy} their mutual interaction. They read:

$$H_y = \epsilon\left(-D\partial_{yy}^2 + \frac{\gamma^2}{4D} y^2 - \frac{\gamma}{2}\right),$$

$$H_x = -D\partial_{xx}^2 + \frac{U'^2}{4D} - \frac{U''}{2} + \frac{\gamma^2}{4D} g^2(\epsilon + g'^2) + \frac{\gamma}{2}\left(\frac{1}{D} g g' U' - g'^2 - g g''\right), \tag{33}$$

$$H_{xy} = \frac{\gamma^2}{4D} g'^2 y^2 - \left[\frac{\gamma^2 g}{2D}(\epsilon + g'^2) + \frac{\gamma}{2}\left(\frac{1}{D} g' U' - g''\right)\right] y.$$

This transformation allows us to take advantage of a Hamiltonian operator whose matrix representation is always symmetric. The underlying idea is to determine the generic basis function element as

$$\psi_{nm} = \varphi_n(y,x)\chi_m(x), \tag{34}$$

where $\varphi_n(y,x)$ are adiabatically displaced eigenfunctions of the harmonic oscillator problem

$$\left\{-D\partial_{yy}^2 + \frac{\gamma^2}{4D}[y - g(x)]^2 - \frac{\gamma}{2}\right\}\varphi_n = \gamma n \varphi_n, \tag{35}$$

while $\chi_m(x)$ are eigenfunctions of the Hamiltonian corresponding to the uncoupled reactive subsystem

$$\left(-D\partial_{xx}^2+\frac{U'^2}{4D}-\frac{U''}{2}\right)\chi_m=\mu_m\chi_m. \tag{36}$$

It is straightforward to construct the matrix representation of the operator H (32) in the basis (34). One obtains

$$\begin{aligned}H_{nm,n'm'}&=(\mu_m+\epsilon\gamma n)\,\delta_{n,n'}\delta_{m,m'}+\gamma n G_{m,m'}\delta_{nn'}\\&\quad+\sqrt{\gamma D(n'+1)}\,\delta_{n,n'+1}R_{m',m}\\&\quad+\sqrt{\gamma D n'}\,\delta_{n,n'-1}R_{m,m'},\\G_{m,m'}&=\langle m|g'^2|m'\rangle,\\R_{m,m'}&=\langle m|e^{U/2D}\partial_x g' e^{-U/2D}|m'\rangle.\end{aligned} \tag{37}$$

The advantage of this representation is that a few basis functions are sufficient to produce very accurate low lying eigenvalues for $\epsilon>\epsilon_c$, and the method is rather insensitive with respect to D and γ. With a decreasing anisotropy parameter the convergence only slowly becomes worse. Even for $\epsilon=10^{-4}\epsilon_c$, just 10–15 basis functions per x and y are typically required to obtain 3–4 significant digits independently of the barrier height and coupling constant. The resulting matrices can easily be diagonalized by standard routines for sparse or band structured matrices. This is in drastic contrast to the conventional basis set of unscaled harmonic oscillator eigenfunctions used so far (see, e.g., Ref. 25). For the present problem, with a conventional basis set, 30–40 unscaled harmonic oscillator basis functions per degree of freedom are necessary to converge to two significant digits even at an intermediate value of the barrier height, say $E=5$, corresponding to $D=0.05$, and critical anisotropy parameter $\epsilon=\epsilon_c$. With further decreasing D or ϵ the convergence becomes much worse, and special methods such as the Lanczos algorithm are necessary, in order to first tridiagonalize the resulting matrices and only then to calculate the first nonzero eigenvalue. We note also that our results are in contrast to the ''intuitive feeling'' expressed by Makri and Miller[26] who warn to use the basis χ_m if one needs to properly incorporate the effect of coupling to the bath.

Now, it remains to evaluate the eigenvalues μ_m, and the matrix elements $G_{m,m'}$ and $R_{m,m'}$ in an economical way. Presently, there are many methods available by which the one-dimensional Schrödinger equation (36) can be solved. Two of them will be discussed below. If the potential $U(x)$ and the force $g(x)$ are polynomials, a good way of doing this is to use a set of scaled harmonic oscillator eigenfunctions

$$\chi_m=\sum_{i=0}^{\infty} C_{m,i}|i\rangle, \tag{38}$$

$$\left(-D\partial_{xx}^2+\frac{\omega^2}{4D}x^2-\frac{\omega}{2}\right)|i\rangle=\omega i|i\rangle, \tag{39}$$

where the frequency ω is a free parameter which can be chosen so that the convergence of the series in Eq. (38) is as fast as possible. The matrix representation of the Hamiltonian (36), as well as a way of determining ω are given in the appendix. Here we only note that an optimal choice of the free parameter ω sensitively depends on the number of basis functions N which are taken into account in the series (38). This problem has already been studied in Ref. 31 with the result that for a given N the optimal value of ω minimizes the trace of the matrix representation of the Hamiltonian (36) in the basis (39) truncated at $i=N-1$. For the present problem this yields [see Eq. (A7)]

$$\omega=(15D^2N^2)^{1/4}. \tag{40}$$

The use of the basis of scaled harmonic oscillator eigenfunctions allows us to decrease the truncation number N, which is necessary to converge to 12 significant digits, at least by a factor of 2 compared to the standard unscaled basis set corresponding to $\omega=1$. Another advantage of the basis (39) is that it permits one to evaluate the matrix elements $G_{m,m'}$ and $R_{m,m'}$ analytically, that is, without loss of accuracy, provided $g(x)$ and $U(x)$ are polynomials. For the potential $U(x)$ defined in Eq. (4) and a linear coupling function $g(x)=x$ a straightforward calculation yields the following algebraic expressions:

$$\begin{aligned}G_{n,m}&=\delta_{n,m},\\R_{n,m}&=\sum_{i=0}^{N-1}\sqrt{i+1}\left\{\sqrt{\frac{D}{4\omega}}\left[\frac{3D}{\omega}(i+1)-1\right]\right.\\&\quad\times(C_{n,i}C_{m,i+1}+C_{n,i+1}C_{m,i})\\&\quad\left.-\sqrt{\frac{\omega}{4D}}\,(C_{n,i}C_{m,i+1}-C_{n,i+1}C_{m,i})\right\}\\&\quad+\frac{(D/\omega)^{3/2}}{2D}\sum_{i=0}^{N-3}\sqrt{(i+1)(i+2)(i+3)}\\&\quad\times(C_{n,i+3}C_{m,i}+C_{n,i}C_{m,i+3}).\end{aligned} \tag{41}$$

We note that this method can be applied to all types of potentials (polynomials or finite sums of exponentials) for which the matrix representation of the Hamiltonian (36) can be determined analytically. If this is not the case, a finite-difference method as described in the next subsection can be used.

We also note that in principle, one could use a basis set which consists of the eigenfunctions $\Phi_m(x,y)$ [see Eqs. (8) and (10)]. The advantages of such a basis are that it explicitly takes into account the coupling, and produces accurate results in the strongly anisotropic limit with just a few basis functions. The main disadvantage of this approach is that the corresponding matrix representation cannot be determined analytically. Rather, one has to solve the x-problem for many different values of y, and then to perform a large number of quadratures numerically. From this point of view the basis which is described above seems preferable. It also incorporates the coupling explicitly and produces a very rapid convergence combined with a minimal computational effort.

B. A finite-difference scheme

The method that we now outline is an application of a finite-difference scheme for the solution of nonlinear time-dependent Smoluchowski equations.[32] Since the present problem is linear and time-independent, the scheme can be

substantially simplified and further improved. In order to simplify notations, we consider the following eigenvalue problem of a one-dimensional Smoluchowski operator:

$$D\partial_x \exp[-U(x)/D]\partial_x \exp[U(x)/D]P(x) = -\mu P(x), \tag{42}$$

where $U(x)$ is assumed to be an arbitrary potential bounded from below and unrestricted from above, so that the corresponding spectrum of eigenvalues is discrete. A generalization to multidimensional cases is straightforward. The key ideas of the method are, first, to represent the associated Hamiltonian operator as a sum of second derivatives, namely,

$$H\psi(x) \equiv D[-\partial_{xx}^2 + e^{U/2D}(e^{-U/2D})'']\psi(x) = \mu\psi(x), \tag{43}$$

where

$$P(x) = \psi(x)\exp\left\{-\frac{U(x)}{2D}\right\},$$

and, second, to introduce a uniformly spaced lattice of N points on the x-axis reading

$$x_i = x_1 + (i-1)h; \quad i = 1,\ldots,N; \quad h = (x_N - x_1)/(N-1),$$

where h denotes the step size. The second derivatives are then approximated by a central difference scheme of the order $2K$ in h

$$(\partial_{xx}^2 F)_i = h^{-2}\left[c_0 F_i + \sum_{j=1}^{K} c_j (F_{i+j} + F_{i-j})\right] + \mathcal{O}(h^{2K}), \tag{44}$$

where $F_i = F(x_i)$, and where the coefficients c_i are determined from[33]

$$c_i = 2(-1)^{i+1}\sum_{j=1}^{K} \frac{[(j-1)!]^2}{(j-1)!(j+i)!}. \tag{45}$$

In this representation, the operator H is a symmetric $(2K+1)$-diagonal matrix whose nonzero elements are given by

$$\begin{aligned} H_{i,i+j} &= H_{i+j,i} = -\frac{D}{h^2} c_j, \quad 1 \leqslant j \leqslant K, \\ H_{i,i} &= \frac{D}{h^2}\sum_{j=1}^{K} c_j e^{U_i/2D}(e^{-U_{i+j}/2D} + e^{-U_{i-j}/2D}). \end{aligned} \tag{46}$$

One might expect that for fixed N this discretization procedure would produce, with increasing K, much more accurate results than obtained with the conventional second order differencing scheme which corresponds to $K=1$. We have found, however, that the use of the matrix H defined by Eq. (46) with $N=31$ leads to a finite first eigenvalue of the Smoluchowski operator varying from 10^{-5} to 10^{-7} instead of exactly being zero. This is because the matrix (46) does not preserve the true ground state solution of the corresponding Hamiltonian operator, or equivalently, satisfy the following condition:

$$(He^{-U/2D})_i = 0, \quad i = 1,\ldots,N. \tag{47}$$

We have found that a dramatic reduction of discretization error is achieved by a simple procedure of computing the diagonal elements so that the ground state solution is preserved. Specifically, we enforce Eq. (47) by the following modification of the diagonal of H:

$$\begin{aligned} H_{i,i} = \frac{D}{h^2}\sum_{j=1}^{K} c_j e^{U_i/2D}[&\xi(N+1-i-j)e^{-U_{i+j}/2D} \\ &+ \xi(i-j)e^{-U_{i-j}/2D}], \end{aligned} \tag{48}$$

where

$$\xi(x) = \begin{cases} 1 & \text{if } x > 0, \\ 0 & \text{otherwise.} \end{cases}$$

The accuracy of a finite-difference approach is typically determined by the accuracy of the space discretization. The standard way to control it is thus by increasing the number of grid points. In practice, however, one would like this number to be as small as possible, in order to achieve computational economy. The advantages of the method presented are, first, that it is an integration free method, and, second, that it allows one to achieve a given level of accuracy with a slow (or even without) increase of the number of grid points solely due to increasing K. Both features are particularly important in studying problems like Eqs. (20) and (13), when the computational effort which is necessary for the evaluation of matrix elements is comparable with the one for its diagonalization.

The method described above has been used for the numerical solution of the one-dimensional problem (20) and (13). It can also be used for solving the two-dimensional problem (4), where its utility, of course, is not restricted solely to a certain kind of system-bath Hamiltonians. We preferred though the variational method for the two-dimensional problem, since it first possesses an upper bound property of the calculated eigenvalues and, second, converges faster than the finite-difference scheme.

IV. RESULTS

The two-dimensional problem has been solved in a wide range of the anisotropy parameter $10^{-6} \leqslant \epsilon \leqslant 10^3$. The coupling constant was varied in the interval $10^{-3} \leqslant \gamma \leqslant 10^2$ at two temperatures $D=0.05$ ($E=5$) and $D=0.025$ ($E=10$). Results for the first nonzero eigenvalue are presented in Tables I and II. We have also numerically solved the one-dimensional Smoluchowski equation (20). We find that our predictions based on this equation agree well with the numerically exact results obtained for the two-dimensional problem. The main findings are as follows.

(i) In the limit of weak coupling (low bath frequency) $\gamma \sim D$, the longtime behavior is governed by a set of low lying equidistant eigenvalues for diffusion anisotropies ϵ smaller than the critical value ϵ_c defined in Eq. (28). These eigenvalues read

$$\lambda_n = \epsilon\gamma n, \quad n = 0,1,\ldots, \tag{49}$$

TABLE I. First nonzero eigenvalue λ_1 for the problem (4). (Exponential notation $-k$ means that the number preceding is to be multiplied by 10^{-k}.)

ϵ	γ=0.1	0.5	1	2	100
		D=0.05	(E=5)		
0.1–5	0.31423-7	0.15156-7	0.71444-8	0.43679-8	0.28010-8
0.1–4	0.31420-6	0.15152-6	0.71436-7	0.43679-7	0.27989-7
0.1–3	0.31390-5	0.15132-5	0.71398-6	0.43670-6	0.27987-6
0.1-2	0.31090-4	0.14969-4	0.71075-5	0.43579-5	0.27962-5
0.1–1	0.28389-3	0.13640-3	0.68109-4	0.42697-4	0.27708-4
0.1	0.14586-2	0.78539-3	0.49776-3	0.35810-3	0.25409-3
1	0.23567-2	0.18389-2	0.16454-2	0.15243-2	0.13909-2
10	0.26242-2	0.25537-2	0.25397-2	0.25320-2	0.25239-2
100	0.27506-2	0.27490-2	0.27488-2	0.27487-2	0.27486-2
1000	0.27734-2	0.27734-2	0.27734-2	0.27734-2	0.27734-2
		D=0.025	(E=10)		
0.1–5	0.13187-7	0.58846-9	0.79619-10	0.34429-10	0.20296-10
0.1–4	0.13063-6	0.58369-8	0.79544-9	0.34426-9	0.19758-9
0.1–3	0.12003-5	0.57252-7	0.79347-8	0.34406-8	0.19768-8
0.1–2	0.70383-5	0.52245-6	0.78482-7	0.34317-7	0.19752-7
0.1–1	0.14886-4	0.32278-5	0.71842-6	0.33455-6	0.19571-6
0.1	0.17133-4	0.84737-5	0.43009-5	0.27128-5	0.17944-5
1	0.17630-4	0.13523-4	0.11895-4	0.10891-4	0.98171-5
10	0.18591-4	0.18045-4	0.17934-4	0.17873-4	0.17809-4
100	0.19411-4	0.19398-4	0.19397-4	0.19396-4	0.19395-4
1000	0.19570-4	0.19570-4	0.19570-4	0.19570-4	0.19570-4

even though the barrier height E is relatively large. For larger coupling constants (i.e., for intermediate and high frequency baths) the relaxation is always single exponential regardless of the value of the diffusion anisotropy. The first three nonzero eigenvalues of the two-dimensional operator (4) as a function of ϵ are shown in Figs. 3, and compared to those of the one-dimensional Smoluchowski operator (20). One sees that the eigenvalues of the two operators coincide over a wide range of ϵ.

(ii) For all values of D and γ the dependence of λ_1 on ϵ changes qualitatively in the vicinity $\epsilon \sim \epsilon_c$. In the limit of strong coupling $\gamma \gg U''(x_{\min})$, the relation (24) always holds, and ϵ_c is close to unity. With decreasing γ the value of ϵ_c also decreases in full agreement with Eq. (27) until $\gamma \sim D$. In the latter case, the potential barrier in $V_e(y)$ vanishes, and since then Eq. (23) becomes inappropriate, one has to use Eq. (28) in order to estimate the critical value ϵ_c. These observations are illustrated by Figs. 3 and Fig. 4 where the first nonzero eigenvalue of Eq. (4) is shown as a function of the anisotropy parameter. For the sake of completeness we also show in Fig. 4 the asymptotic solutions λ_1^{∞} (25) and λ_1^0 (23) obtained in terms of the one-dimensional Smoluchowski equations (2) and (20), respectively. They are seen to agree well with the numerically exact results obtained for the two-dimensional problem for both an intermediate (E=5) and relatively large (E=10) barrier height. Quite remarkable is the fact that the mean first passage time estimate for λ_1^{∞}, Eq. (23), turns out to be not too bad even for $\gamma \sim D$ (e.g., for γ=0.1 and D=0.05) although then the potential $V_e(y)$ has no noticeable barrier (see Fig. 2).

(iii) With further decreasing coupling constant, $\gamma \lesssim D$, ϵ_c begins to grow in accordance with Eq. (28). For $\gamma \sim e^{-E}$ it again reaches unity and continues to increase as $1/\gamma$ when γ goes to zero. In this limit, the spectrum of eigenvalues of the two-dimensional problem (4) becomes similar to the spectrum of a one-dimensional harmonic oscillator (49). Results for the first nonzero eigenvalue in the limit of weak coupling are shown in Table II and Fig. 5.

(iv) As expected, the Langer formula (7) provides quite accurate results in the limit of strong coupling independently

TABLE II. The same as in Table I but for the limit of weak coupling between the system and the bath mode.

	D=0.05			D=0.025		
ϵ	γ=0.001	0.005	0.01	0.001	0.005	0.01
0.1–0.3	0.98161-7	0.45716-6	0.84200-6	0.96238-7	0.41700-6	0.71055-6
0.1–02	0.98160-6	0.45710-5	0.84164-5	0.96072-6	0.40151-5	0.63035-5
0.1–01	0.98155-5	0.45652-4	0.83795-4	0.93132-5	0.17425-4	0.17661-4
0.1	0.98097-4	0.44987-3	0.79228-3	0.19386-4	0.19325-4	0.19215-4
1	0.97225-3	0.25058-2	0.25679-2	0.19553-4	0.19467-4	0.19360-4
10	0.27538-2	0.27465-2	0.27337-2	0.19567-4	0.19486-4	0.19394-4
100	0.27719-2	0.27649-2	0.27605-2	0.19570-4	0.19520-4	0.19487-4
1000	0.27746-2	0.27738-2	0.27735-2	0.19579-4	0.19573-4	0.19571-4

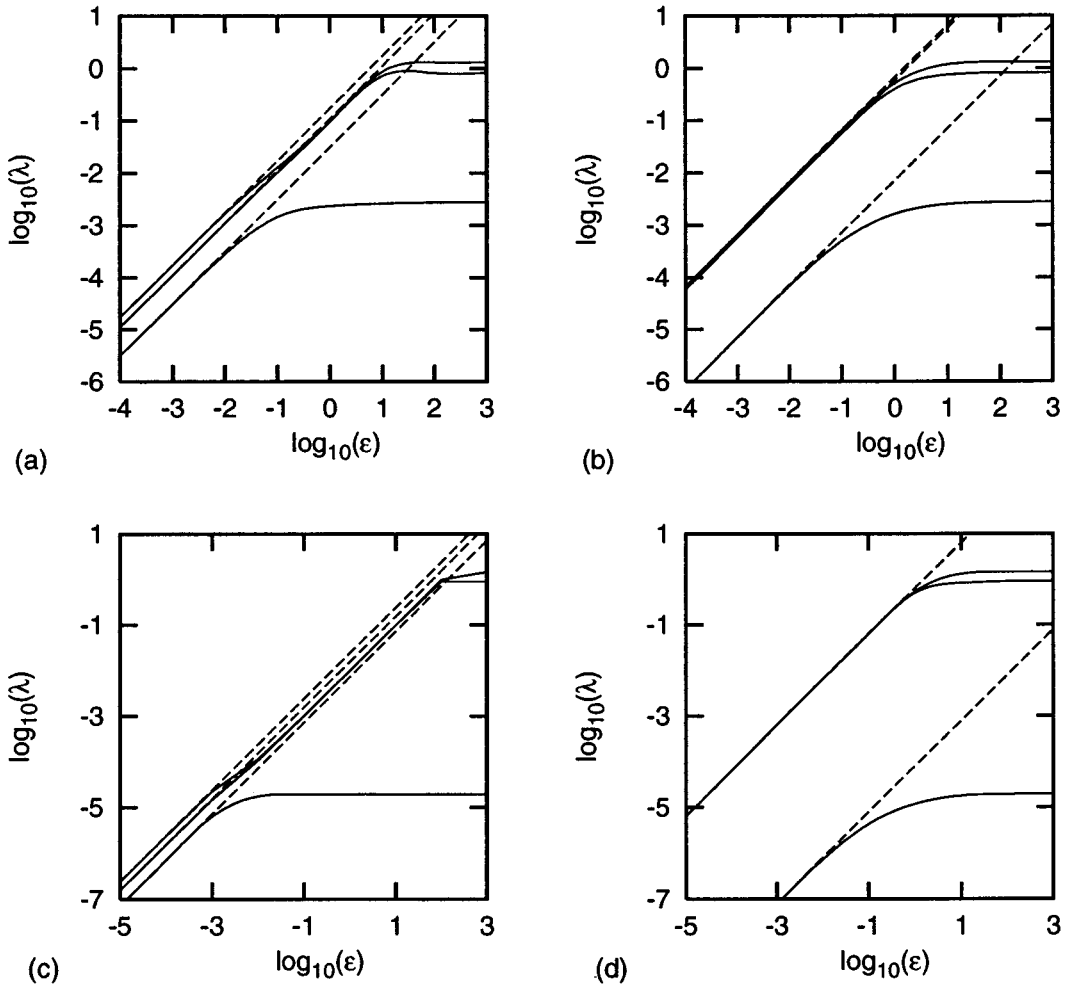

FIG. 3. Logarithm of the first three nonzero eigenvalues of the two-dimensional problem [Eq. (4)] as a function of the anisotropy parameter ϵ. (a) $D=0.05$, and $\gamma=0.1$; (b) $D=0.05$, and $\gamma=1$; (c) $D=0.025$, and $\gamma=0.01$; (d) $D=0.025$, and $\gamma=1$. The dashed lines are for the eigenvalues of the one-dimensional operator, Eq. (20).

of the anisotropy parameter. With decreasing γ the Langer formula still applies for $\epsilon \geqslant \epsilon_c$, and fails otherwise. As is evidenced by Fig. 6, the latter is true for potentials with both single ($\gamma \geqslant 1$) and double ($\gamma < 1$) well profiles $V(x,y=\text{const})$. It turns out that for intermediate barrier height, say $E=5$, and coupling strength $\gamma \sim 1$ the breakdown of the Kramers–Langer theory already sets in in the isotropic regime $\epsilon \sim 1$. Finally, in the limit of weak coupling, $\gamma \sim e^{-E}$ (e.g., for $E=5$, and $\gamma=0.001$), the Kramers–Langer theory fails even for $\epsilon \geqslant 1$. We emphasize that these results are in accordance with the criterion (29) that we derived to check the validity of the Kramers–Langer theory.

V. CONCLUDING REMARKS

In this paper, a rather fast and easily applicable variational method was developed for solving multidimensional Smoluchowski and Schrödinger equations of a system–bath form. The power of the method is illustrated for a two-dimensional problem describing, e.g., charge-transfer reactions in polar solvents. The results are very encouraging since a relatively small number of basis functions can quite accurately account for the effect of the bath on the system in a wide range of the anisotropy parameter reaching from a very fast to an almost frozen bath mode. We have presented numerically exact results for rate constants of a classical symmetric double well system coupled to a dissipative mode. These results allow us to analyze the problem without using ad hoc assumptions in a rather wide range of parameters, as well as to clarify the question of the range of validity of the Kramers–Langer theory. We conclude that for relatively high barriers with strong coupling between the system and the bath mode the Kramers–Langer theory yields results which are accurate for all values of the diffusion anisotropy. Otherwise it may fail grossly even near the isotropic diffusion case. In particular, it turns out that the shapes of the potential profiles at fixed values of y do not play the decisive role that is attributed to them by Berezhkovskii and Zitserman.[15] Our calculations revealed also that Langer's formula for the rate may break down for $\epsilon > 1$ if the coupling constant is sufficiently small.

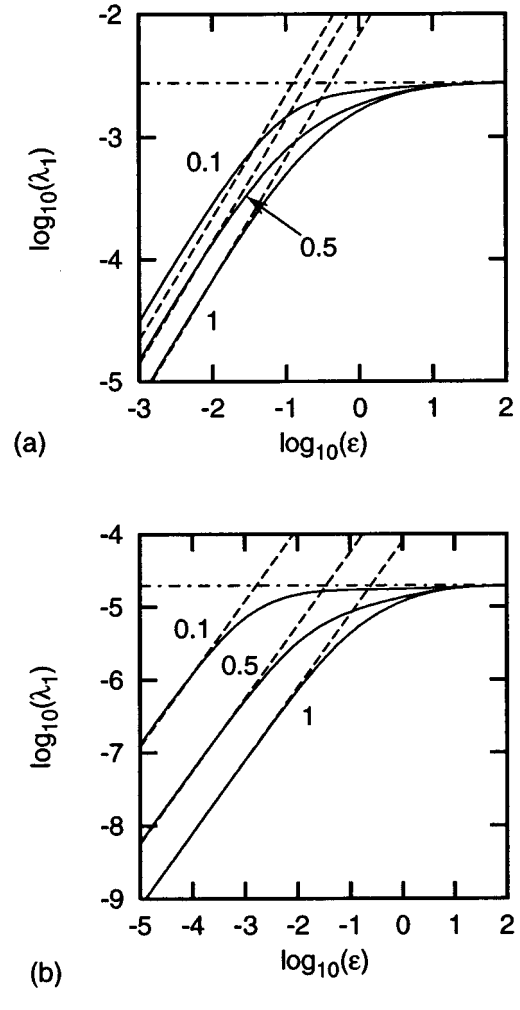

FIG. 4. Logarithm of the first nonzero eigenvalue of the two-dimensional problem [Eq. (4)] as a function of the anisotropy parameter ϵ for $\gamma=0.1$, 0.5, and 1. (a) $D=0.05$; (b) $D=0.025$. The dashed and dashed dotted lines are for the asymptotic solutions γ_1^0 [Eq. (23)] and γ_1^∞ [Eq. (25)], respectively.

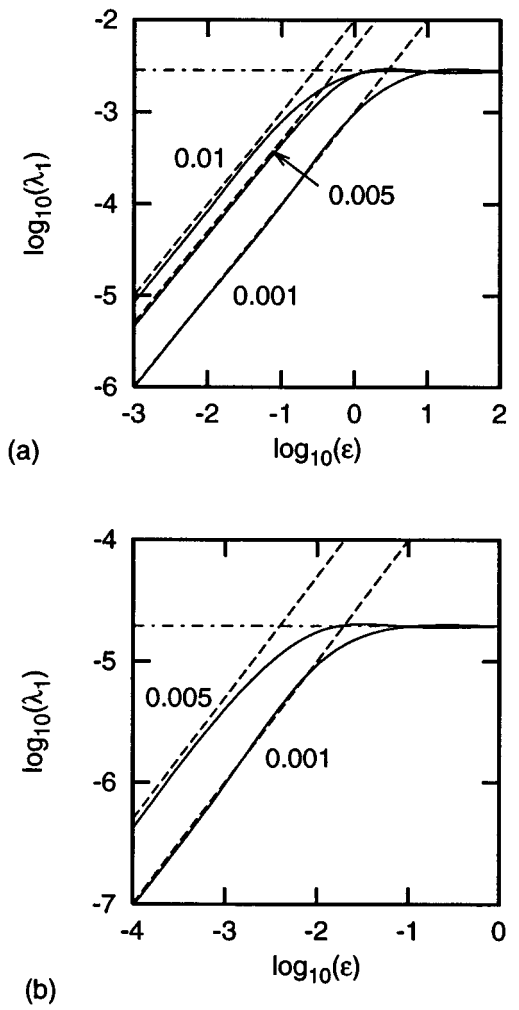

FIG. 5. The same as in Fig. 4 but for $\gamma=0.001$, 0.005, and 0.01. The dashed lines are for the harmonic oscillator asymptotic solution [Eq. (26)].

For strong anisotropy (small ϵ) or weak coupling (small γ) the y coordinate moves slowly compared to x and asymptotically becomes a Markovian process which can be described by a one-dimensional Smoluchowski equation. The comparison of this asymptotic theory with the numerically exact results for the original two-dimensional problem shows excellent agreement nearly up to the isotropic case $\epsilon=1$.

Other aspects of the present model can also be investigated by our method. For instance, one can study the influence of finite barrier corrections of the rate. Another interesting question refers to possible deviations of the stochastic and the deterministic separatrix. These problems presently are under investigation. The present method can also be applied to other relevant problems, such as cases with nonlinear coupling between the system and bath, or spatial dependent diffusion. Finally we note that the Hamiltonian which we have considered, is also suitable for a quantum mechanical description of hydrogen atom transfer reactions.[26] In such a case, no diffusion anisotropy occurs, $\epsilon=1$, and, therefore, one may expect that the method should work even better. We expect that 5–7 basis functions per degree of freedom are sufficient to describe the effect of the bath on the system quite accurately in the whole range of the bath frequency γ. This is particularly advantageous, since the case of the low frequency bath is notoriously difficult in quantum-mechanical calculations.[26] Since the present method admits an obvious generalization to an arbitrary number of bath degrees of freedom, it does not seem to be difficult to study a bath which consists of up to three modes coupled to a system with a reasonable numerical effort.

Note added in proof. After completion of this work we received a preprint by A. M. Berezhkovskii, V. Yu. Zitserman, and A. Polimeno about a related problem with similar results.

ACKNOWLEDGMENTS

We thank Alexander Berezhkovskii and Vladick Zitserman for many stimulating discussions and are grateful to Jens Emmerich for his help in carrying out numerical calculations. This work was supported by the Schweizerischer Nationalfond.

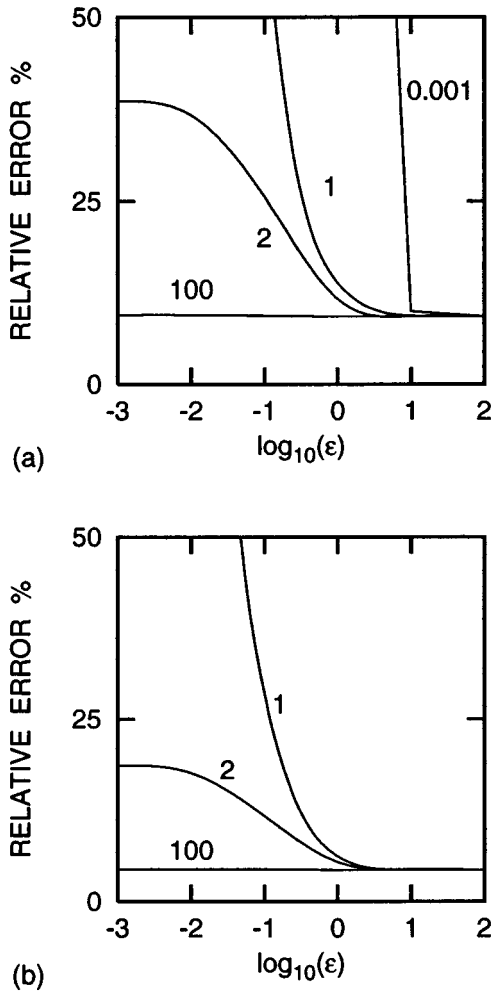

FIG. 6. Relative errors, 100%(approximate-exact)/exact, of the Kramers–Langer formula [Eq. (7)] for $\gamma=0.001$, 1, 2, and 100. (a) $D=0.05$; (b) $D=0.025$.

APPENDIX

The aim of this appendix is to give the matrix representation of the Hamiltonian (36) in the basis (39), and further to show a way of determining the free parameter ω. Just for notational simplicity we rewrite the problem in the conventional form

$$(-\partial_{xx}^2+v_0+v_2x^2+v_4x^4+v_6x^6)\chi_m=E_m\chi_m, \tag{A1}$$

and

$$\left(-\partial_{xx}^2+\frac{\Omega^2}{4}x^2-\frac{\Omega}{2}\right)|i\rangle=\Omega i|i\rangle, \tag{A2}$$

where $E_m=\mu_m/D$, $\Omega=\omega/D$, while the potential coefficients v_m are determined by those of $U(x)$ and D, reading

$$v_0=\frac{1}{2D};\quad v_2=\frac{1}{4D^2}-\frac{3}{2D};\quad v_4=-\frac{1}{2D^2};\quad v_6=\frac{1}{4D^2}.$$

The matrix representation of Eq. (A1) in the basis $|i\rangle$ of Eq. (A2) can easily be found by means of the following well known relations of harmonic oscillator eigenfunctions:

$$\langle i|j\rangle=\delta_{i,j},$$

$$x|i\rangle=\frac{1}{\sqrt{\Omega}}[\sqrt{i}|i-1\rangle+\sqrt{i+1}|i+1\rangle], \tag{A3}$$

$$\partial_x|i\rangle=\frac{1}{2}\sqrt{\Omega}[\sqrt{i}|i-1\rangle-\sqrt{i+1}|i+1\rangle].$$

It has a band structure form, where the diagonals are given by

$$H_{n,n}=v_0+\left(\frac{\Omega}{4}+\frac{v_2}{\Omega}\right)(1+2n)+\frac{3v_4}{\Omega^2}(1+2n+2n^2)+\frac{5v_6}{\Omega^3}(3+8n+6n^2+4n^3),$$

$$H_{n,n-2}=H_{n-2,n}=\sqrt{n(n-1)}\left[-\frac{\Omega}{4}+\frac{v_2}{\Omega}+\frac{2v_4}{\Omega^2}\times(2n-1)+\frac{15v_6}{\Omega^3}(1-n+n^2)\right], \tag{A4}$$

$$H_{n,n-4}=H_{n-4,n}=\sqrt{n(n-1)(n-2)(n-3)}\times\left[\frac{v_4}{\Omega^2}+\frac{3v_6}{\Omega^3}(2n-3)\right],$$

$$H_{n,n-6}=H_{n-6,n}=\frac{v_6}{\Omega^3}[n(n-1)(n-2)(n-3)(n-4)\times(n-5)]^{1/2},$$

while the remaining matrix elements are equal to zero.

It is clear that neither E_m nor χ_m are functions of Ω. But, since we have to truncate the series in Eq. (39) at a finite $i=N-1$ for the numerical treatment, the resulting approximations of the eigenvalues E_m^N and eigenfunctions χ_m^N depend on Ω. So the problem is to determine the free parameter in such a way that the best approximation of the true eigenvalues and eigenfunctions are obtained. A good way of achieving this is to use the upper bound property of the Rayleigh–Ritz method according to which

$$\sum_{m=0}^{N-1}E_m\leqslant\sum_{m=0}^{N-1}E_m^N=\sum_{m=0}^{N-1}H_{m,m}. \tag{A5}$$

Thus minimizing the trace of the Hamiltonian operator in the basis of scaled harmonic oscillator eigenfunctions provides one with a minimal average error of the eigenvalues E_m^N, and, consequently, a reasonable choice of the free parameter for a given number of basis function N. When applied to Eq. (A4), this yields after some lengthy but simple algebra a polynomial of the form

$$\Omega^4-4v_2\Omega^2-8v_4(2N+1/N)\Omega-60v_6(N^2+2)=0, \tag{A6}$$

which is easily solved for Ω when N is large:

$$\Omega=(60v_6N^2)^{1/4}. \tag{A7}$$

Returning in Eq. (A7) to the original notation, one immediately obtains Eq. (40).

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